Sorption of perfluorinated compounds onto different types of sludge

Arvaniti, Olga S.; Andersen, Henrik Rasmus; Nikolaos, Thomaidis S.; Athanasios, Stasinakis S.

Published in:
Programme and Abstract Book Micropol & Ecohazard 2013

Publication date:
2013

Document Version
Publisher's PDF, also known as Version of record

IWA-11634: Sorption of perfluorinated compounds onto different types of sludge

Olga S. Arvaniti[1], Henrik R. Andersen[2], Nikolaos S. Thomaidis[3] and Athanasios S. Stasinakis[1]*

[1]Water and Air Quality Laboratory, Department of Environment, University of the Aegean, University Hill, 81100 Mytilene, Greece

[2]Department of Environmental Engineering, Technical University of Denmark, B113, DK-2800 Kgs Lyngby, Denmark

[3]Laboratory of Analytical Chemistry, Department of Chemistry, University of Athens, Panepistimioupoli Zografou, 15771 Athens, Greece

* corresponding author's email address: astas@env.aegean.gr

Introduction. During the last decade, the occurrence of perfluorinated compounds (PFCs) has been well documented in Sewage Treatment Plants (STPs), worldwide. These compounds present significant research interest due to their global distribution, as well as their persistence, bioaccumulation and potential toxicity [1,2]. Their concentrations in sewage sludge range from some pg g^{-1} to few ng g^{-1} [3,4]. Regarding the occurrence of PFCs in Greece, in a recent study it was reported that their average concentrations ranged up to 6.7 ng g^{-1} dry weight in dewatered sludge [5]. So far, there is few data for their sorption potential to different types of sludge and the mechanisms affecting their sorption [6,7].

Aim of the work. The aim of this research was to investigate the sorption potential of different PFCs to three different types of sludge (primary sludge, secondary sludge and anaerobic digested sludge). The solid - water distribution coefficient (K_d) values for five PFCs (C8-C11 carboxylates and C8 sulfonate) was investigated in laboratory batch experiments. Furthermore, the influence of pH and ion strength on sorption was studied.

Sludge. Different types of sludge (Table 1) were collected from a municipal STP (Athens, Greece), receiving wastewater from domestic and industrial sources. This STP was operated with a hydraulic retention time (HRT) and sludge retention time (SRT) of 9 h and 8 days, respectively. Each portion of sludge was washed twice with tap water, decanted in order to remove water soluble constituents and frozen at -18 ˚C. Afterwards, the sludge was gently freeze-dried in order to preserve its structure and sterilized by heating at 103 ˚C for minimum 3 h.

Characteristics	Primary sludge	Secondary sludge	Digested sludge
Total Suspended Solids (g L^{-1})	7.0	6.0	24.9
Volatile Suspended Solids (g L^{-1})	6.0	5.2	18.3
pH	6.5	6.5	7.5
Conductivity (mS cm^{-1})	1.6	1.1	8.6
Loss On Ignition (%)	82.9	88.5	71.9

Table 1. Characteristics of sludge used in sorption experiments.

Sorption experiments. Initially, sorption experiments were performed to investigate the equilibrium time for each target compound using secondary sludge. For the determination of K_d values, sorption experiments were carried out for six different spiking levels of PFCs (PFCs concentrations ranging from 0.2 ng L^{-1} to 5 ng L^{-1}; sludge concentration: 1 g L^{-1}). Samples were put in polypropylene flasks which were shaken at 250 rpm and 25 ˚C for 15 h. The ambient pH of sludge was stable throughout the experiment. After equilibrium time, samples were filtered and the supernatants were stored at 4 ˚C until analysis. The effect of solution pH on PFCs sorption was investigated in other experiments performed at pH values commonly found in STPs (6, 7 and 8). Finally, the influence of two divalent cations (Ca^{2+}, Na^{+}) on sorption potential of PFCs was evaluated. Except for equilibrium time experiment, all other experiments were performed in triplicate.

Analytical method. Analytes in water samples were extracted with solid phase extraction using Oasis HLB cartridges. In brief, cartridges were preconditioned with 6 mL of methanol and 10 mL of HPLC-grade water. After sample loading, cartridges were washed with 2 mL of 40% methanol in HPLC-grade water and the target compounds were eluted with 4 mL of methanol. HPLC separation was performed on an Agilent-1200 high performance liquid chromatography system (Agilent, Palo Alto, CA, USA). Detection was performed with an Agilent 1100 MSD ion-trap system (Agilent, Palo Alto, CA, USA) using electrospray ionization and measuring in negative ion mode. A 10 μL aliquot of standard solution/sample was injected into a guard column (Luna C18, Phenomenex, 2.0 mm i.d. x 4 mm, 5 μm) which was sequentially connected to a XTerra MS C18 column (2.1 mm i.d. x 100 mm, 3.5 μm; Waters), both held at 25 ˚C. The optimum working conditions were: gradient elution with 5 mM ammonium formate aqueous solution (solvent A) and methanol (solvent B) as mobile phase, starting at 70% methanol and increasing linearly at a flow rate of 100 μL min^{-1}. Operating conditions in the ESI source and the ion trap were: capillary voltage at 3500 V, source temperature at 350 ˚C, drying gas at 8 L min^{-1} and nebulizer gas at 30 psi. Methods' limits of quantifications (LOQs) of the target compounds varied from 58.2 ng L^{-1} (Perfluoroundecanoic acid; PFUdA) to 197.3 ng L^{-1} (Perfluorodecanoic acid; PFDA).

Results. According to the results, the sorption equilibrium time of the target compounds was reached within 15 h. The sorption of PFCs onto sludge was different between target compounds. Higher removal during equilibrium experiment (Figure 1) and higher K_d values were observed for long chain PFCs (e.g. Perfluorodecanoic acid; PFDA, PFUdA) and for Perfluorooctane sulfonate (PFOS). This observation is consistent with previous studies reporting that the length of the perfluorocarbon tail and the functionality of the head group can affect sorption to sludge and sediment.

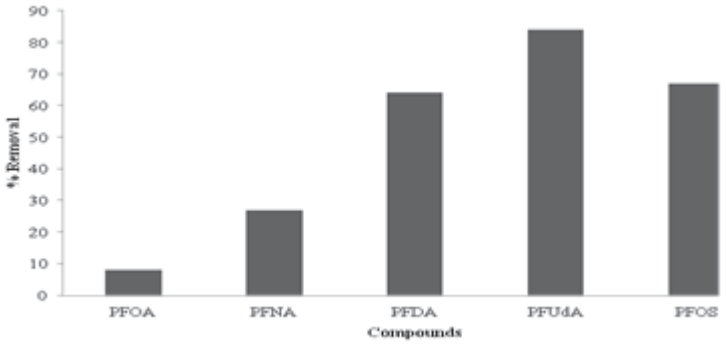

Figure 1. PFCs removal from equilibrium experiment using 1.0 g L^{-1} secondary sludge (time: 15h).

As shown in Figure 2, the removal of analytes decreased with the increase of pH. On the other hand, increase of Ca^{2+} concentration improved sorption of PFCs, while no significant effect was observed for different Na^{+} concentrations.

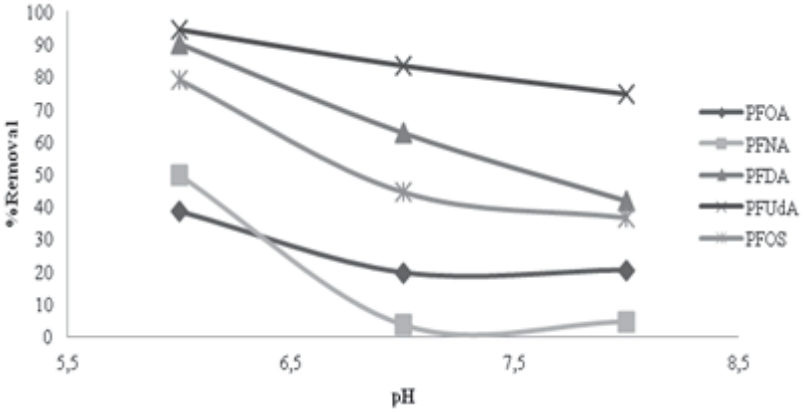

Figure 2. Effect of pH on the removal of PFCs by 1.0g L^{-1} secondary sludge.

References

L. Ahrens. (2011) Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate. *Journal Environmental Monitoring* 13 (1), 20-31.

S. Rayne, K. Forest. (2009) Perfluoroalkyl sulfonic and carboxylic acids: A critical review of physicochemical properties, levels and patterns in waters and wastewaters, and treatment methods. *Journal of Environmental Science and Health Part A* 44 (12), 1145-1199.

C.P. Higgins, J.A. Field, C.S. Criddle, R.G. Luthy. (2005) Quantitative determination of perfluorochemicals in sediments and domestic sludge. *Environmental Science & Technology* 39 (11), 3946-3956.

E. Sinclair, K. Kannan. (2006) Mass loading and fate of perfluoroalkyl surfactants in wastewater treatment plants. *Environmental Science & Technology* 40 (5), 1408-1414.

O.S. Arvaniti, E.I. Ventouri, A.S. Stasinakis, N.S. Thomaidis. (2012) Occurrence of different classes of perfluorinated compounds in Greek wastewater treatment plants and determination of their solid-water distribution coefficients. *Journal of Hazardous Materials* 239-240, 24-31.

Q. Zhou, S. Deng, Q. Yu, Q. Zhang, G. Yu, J. Huang, H. He. (2010) Sorption of perfluorooc*tane sulfon*ate on organo-montmorillonites. *Chemosphere* 78 (6), 688-694.

V. Ochoa-Herrera, R. Sierra-Alvarez. (2008) Removal of perfluorinated surfactants by sorption onto granular activated carbon, zeolite and sludge. *Chemosphere* 72 (10), 1588-1593.

Acknowledgement

"This project was implemented under the Operational Program «Education and Lifelong Learning» and funded by the European Union (European Social Fund) and National Resources – HRAKLEITOS II."

Programme and Abstract Book

Micropol & Ecohazard 2013

16-20 June, 2013
Zurich, Switzerland

8th IWA Specialized Conference on «Assessment and control of micropollutants and hazardous substances in water»

International Water Association

www.micropol2013.ch

eawag aquatic research